(Trimethoxysilyl)carbene: Photochemistry, Oxidation, and Carbonylation of a Silylcarbene

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Photolysis ($\lambda > 345$ nm) of matrix-isolated (trimethoxysilyl)diazomethane (**1e**) leads to the formation of (trimethoxysilyl)carbene (**2e**), which was characterized by IR and UV−vis spectroscopy. The photochemistry, reaction with molecular oxygen, and carbonylation of **2e** were studied in argon matrices at cryogenic temperatures. These experiments demonstrate that **2e** is a triplet ground state carbene. Photolysis at 280 nm results in the formation of 1,1-dimethoxy-1,2-silaoxetane by insertion of the carbene center into one of the adjacent methyl groups.
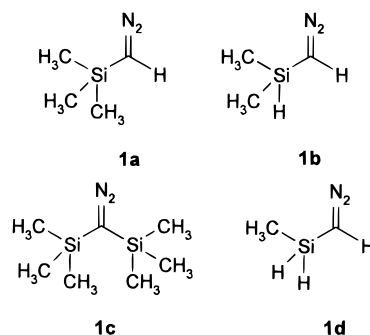
Introduction

Alkyl- and arylsilylcarbenes **2** are highly reactive molecules which rapidly rearrange to silenes **3** via [1,2]-migration of hydrogen, alkyl, or silyl groups.[1] The
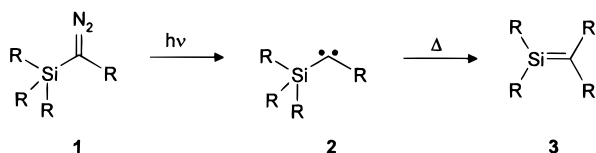
rearrangement of cyclic silylcarbenes provides an entry to silabenzenes.[2] Since carbenes **2** are readily produced from diazomethanes **1**, this reaction is frequently used as an effective route for the generation of silenes **3**.[3−12]

Direct spectroscopic evidence for silylcarbenes is scarce.[13] Chedekel et al. reported the photolysis of (trimethylsilyl)diazomethane (**1a**), (dimethylsilyl)diazomethane (**1b**), and bis(trimethylsilyl)diazomethane (**1c**) in solid argon at 10 K, which resulted in the formation of traces of the corresponding carbenes **2a**−**c**.[5] The carbenes were characterized as linear ground state triplets by ESR spectroscopy. IR spectroscopic observation of **2a**−**c** failed,[4,5] since either the carbenes are not photostable under the conditions required to photolyse the diazo precursor or the activation barrier for the [1,2]-

migration is so low that even at cryogenic temperatures the rearrangement is fast.

Indirect evidence for carbenes **2** comes from trapping experiments with alcohols, alkenes, etc.[1] In O_2-doped argon matrices irradiation of **1b**,**d** produced silyl formates **6b**,**d**. A plausible mechanism for the formation of **6** involves the thermal addition of O_2 to carbene **2**, photochemical rearrangement of the highly photolabile carbonyl *O*-oxide **4**, and a second rearrangement of the dioxirane **5** to finally give **6** (Scheme 1). This reaction sequence is frequently used for the identification of matrix-isolated carbenes.[13,14]

To avoid the [1,2]-shift and to obtain silylcarbenes **2** in higher yields, substituents with a low migratory aptitude at the silicon atom must be used. We report here the chemistry and spectroscopic characterization of a trimethoxy-substituted silylcarbene.

Results and Discussion

Photochemistry of (Trimethoxysilyl)diazomethane (1e). Diazomethane **1e** is synthesized by the reaction of trimethoxysilyl triflate with diazomethane and purified by preparative gas chromatography. Irradiation of matrix-isolated (Ar, 10 K) **1e** with $\lambda > 345$ nm for several hours results in complete disappearance of the diazo compound. The major photoproduct exhibits weak UV absorption maxima at 310, 317, 324, and 332 nm and a weak IR absorption at 1641 cm^{-1}, characteristic[15] of a diazirine chromophore, and is

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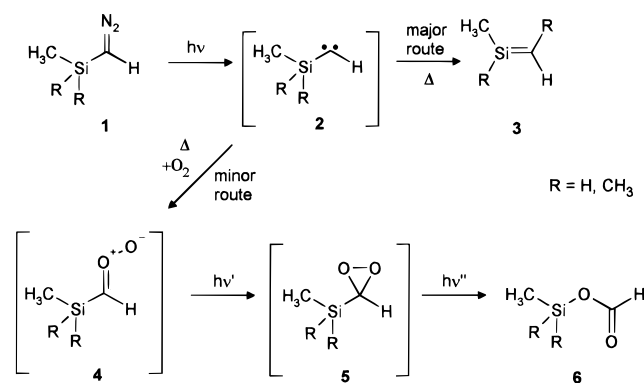(14) Sander, W. *Angew. Chem.* **1990**, *102*, 362; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344.
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Scheme 1

Table 1. IR Spectroscopic Data for Silaoxetane 8

no.[a]	argon, 10 K		ab initio RHF//6-31G(d,p)		assignt[d]
	ν, cm^{-1}	I^b	ν, cm^{-1} ^{c}	I^b	
48	2999.1	10	2965	7	C−H str
46	2982.1	11	2953	10	C−H str
44	2958.9	10	2937	10	C−H str
43			2927	10	C−H str
41	2916.7	9	2898	15	C−H str
40			2873	13	C−H str
39	2858.6	8	2865	13	C−H str
33			1462	1	H−C−H bend
31	1414.7	3	1424	3	H−C−H bend
30	1309.1	3	1328	3	H−C−H rock
28	1202.9	29	1193	22	CH$_3$ rock
27	1197.5	29	1188	23	CH$_3$ rock
23	1125.9	51	1131	59	asym Si−C−O str
22			1122	14	asym Si−C−O str
21	1104.1	100	1112	100	asym Si−C−O str
	942.2	3			
20	921.9	37	968	27	C−O ring str
19	911.2	10	913	2	C−C ring str
18	907.4	30	887	24	ring deform
17	887.0	21	874	30	CH$_2$ twist
16	822.6	18	796	18	CH$_2$ rock
15	768.0	18	742	19	
14	732.4	11	708	13	Si−C str
12	530.7	4	511	5	O−Si−O bend

[a] Number of vibrational mode. The assignment of experimental to calculated vibrations is based on the comparison of band positions and relative intensities. Calculated vibrations with relative intensities lower than 0.5 are omitted in this table. [b] Relative intensities based on the most intense band (100%). [c] Calculated frequencies are scaled by 0.90. [d] Approximate description.

therefore assigned to structure **7**. The rearrangement **1e** → **7** is reversible, and at 305 nm irradiation small amounts of the diazomethane **1e** ($\nu_{N=N}$ 2089 cm^{-1}) are re-formed. This is in accordance with the photochemistry of other silyldiazomethanes[4,5,12] and confirms the assignment of **7**. A minor product at 345 nm irradiation, and the major product at 305 nm irradiation, is (trimethoxysilyl)carbene (**2e**). Prolonged 305 nm irradiation results in the formation of **2e** as the only product observed by IR spectroscopy. The carbene exhibits UV absorptions at 240−265 nm (tailing) and the most intense IR absorptions at 1120, 1108, and 852 cm^{-1}. The assignment is based on the subsequent reaction of **2e** with molecular oxygen and carbon monoxide (vide infra).

Short-wavelength UV irradiation ($\lambda > 280$ nm) of **2e** leads to a single compound with the most intense IR absorption at 1104 cm^{-1} (Table 1, Figure 1). By comparison with *ab initio* calculations at the RHF/6-31G(d,p) level of theory[16] the new compound was assigned the structure of 1,1-dimethoxy-1,2-silaoxetane (**8**; Scheme 2). The IR spectra of two other isomers of
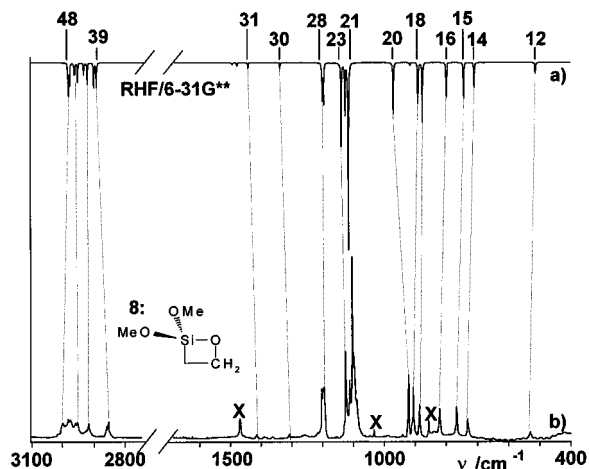

Figure 1. IR spectra of 1,1-dimethoxy-1,2-silaoxetane (**8**), matrix isolated in argon at 10 K (bottom, b) and ab initio calculated at the RHF/6-31G(d,p) level (top, a). Tentative assignments are based on band positions and intensities. The calculated spectrum is scaled by a factor of 0.9 to allow direct comparison with the experimental spectrum, and a Lorentz band shape is simulated with a half-width of 2 cm^{-1}. The bands labeled with X are assigned to the solvent. The numbers in the ab initio spectrum correspond to those in Table 1.

Scheme 2
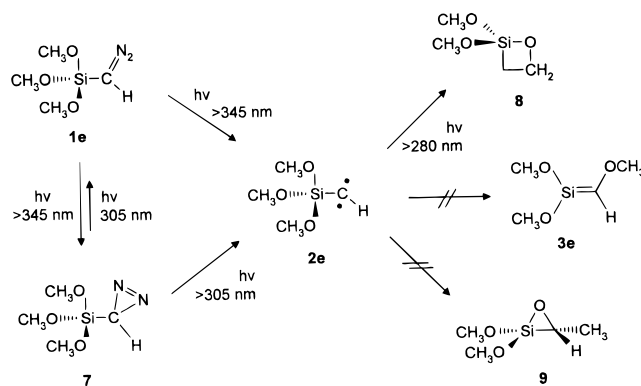
2e (silene **3e** and oxasilirane **9**) were calculated at the same level of theory and were not in agreement with the experimental spectrum. According to these calculations **3e** and **9** are 87 and 28.4 kcal/mol, respectively, higher in energy than **8**. Thus, as expected, the migration of a methoxy group and formation of silene **3e** cannot compete with intramolecular C−H insertion to give **8**. Silaoxetanes are intermediates in the [2 + 2] cycloaddition of silenes and carbonyl compounds[8,17] and are unstable at room temperature if not protected by sterically demanding substituents.[18−23] The formation

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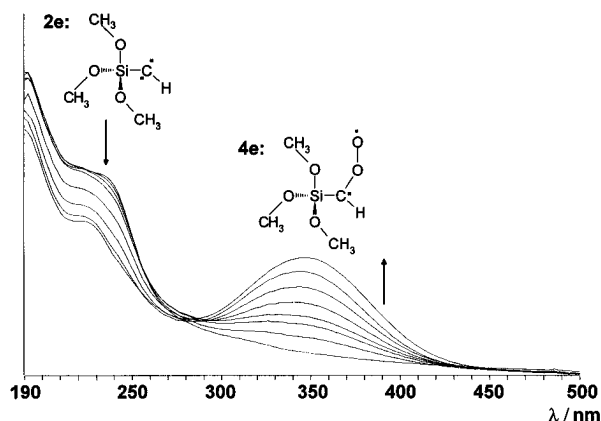(22) Märkl, G.; Horn, M. *Tetrahedron Lett.* **1983**, *24*, 1477.

Figure 2. UV−vis spectra showing the thermal oxidation of silylcarbene **2e** in a 1% O_2-doped argon matrix during warmup from 10 to 45 K. The newly appearing broad absorption (λ_{max} 347 nm) is assigned to trimethoxyformylsilane *O*-oxide (**4e**).

of **8** from **1e** provides a new method for the synthesis of silaoxetanes.

Oxidation of (Trimethoxysilyl)carbene (2e). If diazomethane **1e** is irradiated ($\lambda > 305$ nm, argon/oxygen, 10 K) in a 1% O_2-doped argon matrix, carbene **2e** is still the major product. Small amounts of CO_2, CO, and trimethoxysilyl formate (**6e**) were identified by comparison with authentic matrix-isolated reference compounds. These byproducts are formed by photooxidation of **1e** with O_2 (statistically distributed in argon) located in the same matrix cage. Annealing of the matrix for several minutes at 40 K results in a decrease of **2e** and formation of carbonyl *O*-oxide **4e** in approximately 70% yield. Prolonged annealing does not increase the yield of **4e**. The rapid reaction of **2e** and $^3O_2$ indicates that the ground state of the carbene is triplet.[13]

The IR spectrum of **4e** exhibits the strong and characteristic[14] IR absorption at 918 cm^{-1} assigned to the O−O stretching vibration. $^{18}O_2$ labeling results in a red shift of 49 cm^{-1}, which confirms this assignment. The position of the O−O stretching vibration in carbonyl *O*-oxides depends much on the electronic properties of the substituents, with π-electron-accepting groups leading to blue shifts.[14,24] Since the position of the O−O stretching vibration of **4e** is slightly higher in frequency than that of benzophenone *O*-oxide (896 cm^{-1})[25] and benzaldehyde *O*-oxide (915 cm^{-1}), the trimethoxysilyl group acts as a weakly electron accepting group.

The second characteristic spectroscopic feature of a carbonyl oxide is a broad and strong absorption in the visible region of the spectrum (benzophenone oxide: λ_{max} 422 nm),[26] which also depends on the electronic properties of the substituents.[14] Extended π-systems and electron donors lead to red shifts, while electron acceptors result in blue shifts (trifluoroacetophenone oxide: λ_{max} 378 nm).[27] The absorption maximum of **4e** is observed at 347 nm (Figure 2), which again indicates that the trimethoxysilyl group is electron accepting in a carbonyl *O*-oxide.
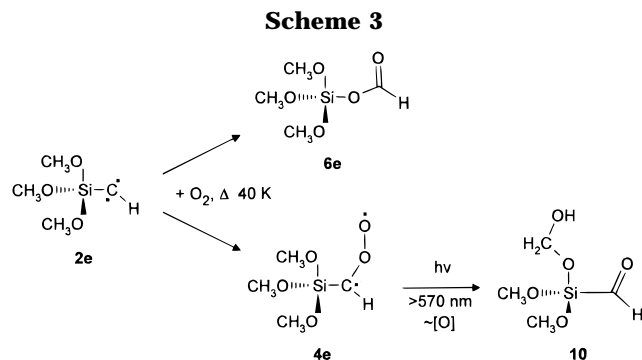
Scheme 3

Carbonyl oxide **4e** is very photolabile, and irradiation with red light ($\lambda > 570$ nm) selectively leads to the disappearance of all IR absorptions assigned to **4e**. A new compound is formed with characteristic IR absorptions at 3450 cm^{-1} (O−H stretching vibration), 2680 cm^{-1} (aldehyde C−H stretching vibration), and 1660 cm^{-1} (aldehyde C=O stretching vibration). This assignment was confirmed by ^{18}O labeling, and the new compound is tentatively assigned to the structure of formylsilane **10** (Scheme 3). Other products, and particularly dioxirane **5e**, were not observed. Thus, the photochemistry of **4e** is different from that of most other carbonyl *O*-oxides, which readily rearrange to dioxiranes.[14] In some cases (e.g., benzaldehyde *O*-oxide)[25] the photochemical cleavage of the O−O bond with formation of the corresponding carbonyl compound is the main reaction. A reasonable mechanism for the formation of **10** is cleavage of the O−O bond in **4e** and subsequent insertion of the O atom into a C−H bond of one of the methoxy substituents.

Photocarbonylation of (Trimethoxysilyl)carbene (2e). A reaction which is frequently used to identify matrix-isolated carbenes is the reaction with CO to produce ketenes.[13,28] Irradiation ($\lambda > 305$ nm, argon/CO, 10 K) of diazomethane **1e** in 3.5% CO-doped argon matrix produced only small amounts of carbene **2e** and new IR absorptions of a compound which was assigned to the structure of ketene **11**. Annealing of
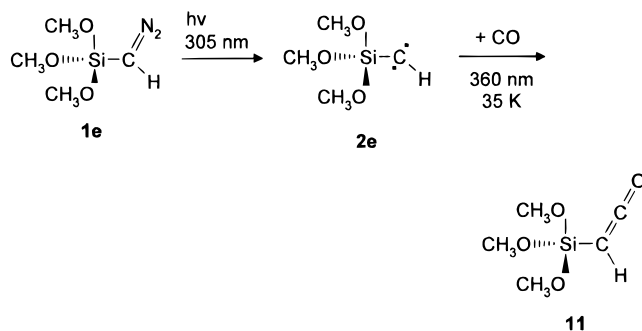
the matrix at 45 K did not increase the yield of **11**. However, irradiation ($\lambda > 360$ nm) at 35 K resulted in the complete disappearance of the carbene and formation of **11**. The IR spectrum of **11** is in good agreement with the RHF/6-31G(d,p) calculated spectrum (Table 2, Figure 3). The most intense absorptions at 2127 and 1100 cm^{-1} are assigned to the C=C=O and Si−O−C stretching vibrations, respectively.

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Table 2. IR Spectroscopic Data for Ketene 11

no.[a]	argon, 10 K		ab initio RHF//6-31G(d,p)		assign[d]
	ν, cm^{-1}	I[b]	ν, cm^{-1} [c]	I[b]	
	3047.7	2			C–H str
	3002.5	4			C–H str
52	2953.7	7	2951	3	C–H str
51			2948	4	C–H str
45	2854.8	7	2863	6	C–H str
44	2126.7	43	2122	100	C=O str
34	1284.3	4	1288	9	
33	1194	32	1193	5	CH$_3$ rock
31/32			1189	7	CH$_3$ rock
27			1127	14	asym Si–C–O str
26	1109.1	sh	1113	33	asym Si–C–O str
25	1100.4	100	1111	34	asym Si–C–O str
	1022.6	2			
	849.8	14			
23	828	8	826	11	
	816.4	5			
22			793	14	
21	784.9	8	760	17	
20	682.7	2	655	1	
19	566.8	1	596	5	
18	551.8	3	533	2	
	481.9	2			
17	477.5	3	494	3	

[a] Number of vibrational mode. The assignment of experimental to calculated vibrations is based on the comparison of band positions and relative intensities. [b] Relative intensities based on the most intense band (100%). [c] Calculated frequencies are scaled by 0.90. [d] Approximate description.
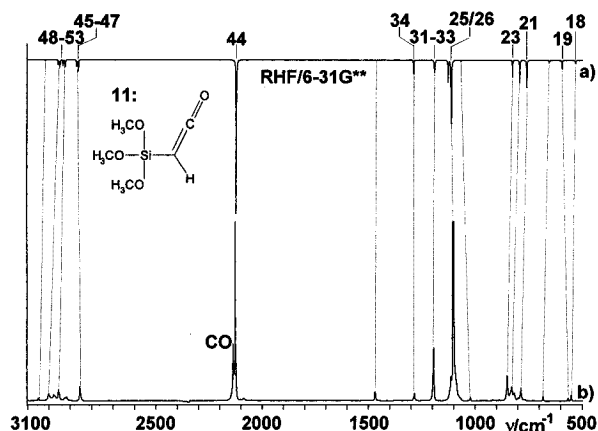

Figure 3. IR spectra of (trimethoxysilyl)ketene (**11**), matrix isolated in argon at 10 K (bottom, b) and ab initio calculated at the RHF/6-31G(d,p) level (top, a). Tentative assignments are based on the band position and band intensity. The calculated spectrum is scaled by 0.9 to allow direct comparison with the experimental spectrum, and a Lorentz band shape is simulated with a half-width value of 2 cm^{-1}. The numbers in the ab initio spectrum correspond to those in Table 2.

Conclusion

Methoxy groups at silicon do not migrate to an adjacent carbene center, and thus (trimethoxysilyl)-carbene can be generated in low-temperature matrices. The carbene reacts thermally with molecular oxygen at cryogenic temperatures, which indicates a triplet ground state. The primary product of the oxygenation is a carbonyl *O*-oxide with typical spectroscopic and photochemical properties. On shorter wavelength UV irradiation the carbene rearranges to a 1,2-silaoxetane. This carbene rearrangement provides a new access to the silaoxetanes.

Experimental Section

Calculations. The *ab initio* calculations were carried out using Gaussian 92[16] and standard basis sets on an IBM RS/6000 workstation. Geometry optimization and frequency calculations were performed at the RHF/6-31G(d,p) level of theory.

Materials and General Methods. ^{1}H and ^{13}C NMR spectra were taken at 400.1 and 100.6 MHz, respectively (Bruker AM 400), in CDCl$_3$ as solvent. Mass spectra (EI, 70 eV) were taken on a Varian MAT CH7 or MAT 8222. All reactions involving moisture-sensitive silicon reactants were performed under an atmosphere of dry nitrogen or argon. All matrix-isolated compounds were purified by preparative-scale GLC using a Shimadzu GC-8a or a Siemens RGC 202 gas chromatograph with a 4 m SE30 column.

Trimethoxysilyl Triflate. Trifluoromethanesulfonic acid (12.16 g, 81.0 mmol) was added dropwise to 16.02 g of neat trimethoxyphenylsilane (80.79 mmol) at room temperature. After complete addition, the reaction mixture was stirred for 1 h at 80–90 °C. Benzene (formed as coproduct) was slowly removed under vacuum at 0 °C. Trimethoxysilyl triflate (11.46 g, 52.3%) was obtained after distillation of the residue under reduced pressure (48–50 °C/8–6 Torr). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.67 (s, 9 H, OCH$_3$).

(Trimethoxysilyl)diazomethane (1e). 1e was synthesized in analogy to the procedure of Martin for the synthesis of (trimethylsilyl)diazomethane.[29] Freshly prepared trimethoxysilyl triflate (30.0 mmol, 8.13 g) was added dropwise to a solution of 1.9 g of diazomethane (45.29 mmol) in 140 mL of diethyl ether and 4.0 g of ethyldiisopropylamine (30.95 mmol) at −40 °C. After complete addition the reaction mixture was stirred for 1 h at −35 °C. The mixture was warmed to −10 °C. The white ammonium salt which precipitated during the reaction was removed by rapid filtration through a frit. The faintly yellow mixture was concentrated in a first step at −40 to −50 °C *in vacuo* in order to remove excess diazomethane. In a second step the solution was carefully concentrated by distillation to about 10 mL (bath temperature was held below 60 °C). The remaining mixture was purified by preparative GLC (SE30, 4 m, 100 °C, detector/injector 140 °C). **1e** (1.25 g, 25.7%) was obtained as a faintly yellow liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.53 (s, 9 H, OCH$_3$), 2.71 (s, 1 H, CN$_2$H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 50.9 (q), 15.7 (d). MS (*m/e* (relative intensity)): 162 (14) [M$^+$], 134 (4) [M$^+$ − N$_2$], 131 (6) [M$^+$ − (OCH$_3$)], 119 (48), [M$^+$ − (N$_2$ + CH$_3$)]. UV−vis (2-methylbutane): λ_{max} 380 nm. IR (Ar, 10 K): 3049 (1), 3000 (5), 2977.7 (4), 2954.6 (7), 2922.2 (3), 2855.7 (8), 2103.9 (9), 2088.8 (100), 1287.1 (3), 1276.7 (14), 1195.2 (19), 1113.3 (17), 1105.7 (100), 1101.4 (100), 851.5 (8), 826.4 (6), 801.5 (2), 787.8 (6), 784.5 (12), 672.8 (3), 551 (0.5), 521.8 (7), 456.1 (5) cm^{-1} (relative intensity). HRMS: calcd for C$_4$H$_{10}$N$_2$O$_2$Si 162.046 000, found 162.046 071 ± 0.4 ppm.

Trimethoxysilyl Formate (6e). A solution of 1.47 g of formic acid (31.92 mmol) in 10 mL of dry diethyl ether was added dropwise to a mixture of 5 g of chlorotrimethoxysilane (31.92 mmol) and 4.13 g of ethyldiisopropylamine (34.96 mmol) in 45 mL of dry ether. After the mixture was stirred for 1 h at room temperature, the precipitated ammonium salt was filtered and washed with dry ether. The filtrate was concentrated by distillation (bath temperature was held below 65 °C). The remaining mixture was purified by distillation under reduced pressure. Silyl formate **6e** (3.67 g, 69.1%) was obtained (83 °C/70 mbar). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.00 (s, 1 H, COOH), 3.55 (s, 9 H, OCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 158.4 (d), 51.5 (q). EI-MS (*m/e* (%)): 166 (16) [M$^+$], 135 (100) [M$^+$ − OCH$_3$], 121 (10) [M$^+$ − COOH], 107 (46). IR (Ar, 10 K): 3006.6 (6), 2997.5 (5), 2938.4 (2), 2921 (1), 1738.6 (78), 1734.9 (35), 1213 (25), 1187.5 (72), 1123.1 (100), 1120.1 (89), 1117.3 (80), 865.4 (25), 853 (13), 797.3 (3), 793.8 (5), 784.8 (28), 756.5 (3) cm^{-1} (relative intensity).

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Matrix Spectroscopy. Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed cycle helium cryostat. Matrices were produced by deposition of argon (Linde, 99.9999%) or mixtures of argon and oxygen (Messer Griesheim, 99.998%) on top of a CsI (IR) or sapphire (UV−vis) window at a rate of approximately 0.15 mmol/min. Infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer with a standard resolution of 1 cm^{-1} in the range 400−4000 cm^{-1}. Irradiations were carried out with use of Osram HBO 500 W/2 mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10 cm path of water. For broad-band irradiation Schott cutoff filters were used (50% transmission at the wavelength specified); for narrow-band irradiation, interference filters in combination with dichroic mirrors ("cold mirrors") and cutoff filters were used.

(Trimethoxysilyl)diazirine (7). Irradiation ($\lambda > 345$ nm, Ar, 10 K) of matrix-isolated (trimethoxysilyl)diazomethane (**1e**) resulted in the formation of (trimethoxysilyl)diazirine (**7**) in a photostationary equilibrium. IR (Ar, 10 K): 3003 (11), 2975.7 (14), 2953.4 (15), 1641.4 (7), 1298 (9), 1195.2 (49), 1119 (34), 1116.2 (46), 1112.9 (46), 1101.5 (100), 977.1 (8), 966.2 (24), 852.4 (30), 830.2 (24), 767.6 (21), 645.7 (3), 460.2 (19) cm^{-1} (relative intensity). UV (Ar, 10 K): λ_{max} 310, 317, 324, 332 nm.

(Trimethoxysilyl)carbene (2e). Shorter wavelength irradiation ($\lambda > 305$ nm, Ar, 10 K) of **1e** or **7** produced (trimethoxysilyl)carbene (**2e**). IR (Ar, 10 K): 2997.1 (11), 2976.3 (13), 2954.7 (15), 2855.1 (16), 2851.6 (13), 1194.8 (53), 1120.1 (34), 1107.9 (100), 851.7 (37), 837 (13), 830.8 (11), 819.5 (14), 425.4 (11) cm^{-1} (relative intensity). UV (Ar, 10 K): λ_{max} tailing from 238 to 265 nm.

1,1-Dimethoxy-1,2-silaoxetane (8). Irradiation ($\lambda > 295$ nm, Ar, 10 K) of matrix-isolated (trimethoxysilyl)carbene (**2e**) finally produced 1,1-dimethyl-1,2-silaoxetane (**8**) in a smooth reaction. IR data: Table 1.

Trimethoxyformylsilane *O*-Oxide (4e). Annealing of matrix-isolated silylcarbene **2e** in a 1% O$_2$-doped argon matrix from 10 to 45 K gave a mixture of silyl formate **6a** and trimethoxyformylsilane *O*-oxide (**4e**). **4e**: IR (Ar, 10 K) 1351.8 (4, 0.991), 1338.9 (6, 0.999), 1270.8 (4, 0.978), 1117.4 (100, 0.994), 1100 (sh, 0.998), 955.5 (17, 0.949), 868.5 (19, 0.999), 799 (20, 0.995), 688.4 (6, 0.997), 492.7 (12, 0.987) cm^{-1} (relative intensity, ratio of ^{18}O/^{16}O isotopic frequencies ν_i/ν); UV (Ar, 10 K) λ_{max} 347 nm.

Dimethoxy(hydroxymethoxy)formylsilane (10). Irradiation ($\lambda > 570$ nm, 10 K) of matrix-isolated **4e** produced dimethoxy(methoxyhydroxy)formylsilane (**10**). IR (Ar, 10 K): 3450.3 (8, 0.996), 2891.1 (1, 1.0), 2679.6 (2, 0.998), 1659.6 (4, 0.978), 1397.9 (1, 0.999), 1375.2 (2, 0.997), 1122.4 (82, 1.0), 1113.1 (100, 1.0), 1034.5 (30, 0.996), 887.5 (21, 1.0), 650.4 (3, 0.996), 596.5 (3, 1.0), 535.2 (4, 0.983) cm^{-1} (relative intensity, ratio of ^{18}O/^{16}O isotopic frequencies ν_i/ν).

(Trimethoxysilyl)ketene (11). Irradiation ($\lambda > 305$ nm, Ar, 10 K) of matrix-isolated (trimethoxysilyl)diazomethane (**1e**) in 3.5% CO-doped argon matrix produced (trimethoxysilyl)-ketene (**11**). IR data: Table 2.